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POLAROGRAPHY WITH STATIONARY ELECTRODES

by

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POLAROGRAPHY WITH STATIONARY ELECTRODES

By L. B. Rogers

ABSTRACT

Mixtures of ions which react rapidly with mercury usually cannot be analyzed polarographically with the dropping mercury electrode. However, these polarographic analyses appear to be feasible using solid electrodes made from noble metals. The general features of their behavior are covered in this report. My collaborators in carrying out this work were A. F. Stehney, R. B. Goodrich, and H. H. Miller.

INTRODUCTION

Polarographic reactions are fundamentally electrolytic processes although polarography as a name attached to the use of micro electrodes to obtain current-voltage curves for analytical purposes was first proposed in 1922. Until just before the last war, polarographic studies were confined almost entirely to the use of the dropping mercury electrode. This was natural because many elements are readily reduced from one oxidation state to another and because mercury with its high hydrogen overvoltage enables one to examine many of these cathode reaction potentials to −1.5 v or more (vs a saturated calomel electrode). However, the reactions which can be studied are usually limited to those which occur at a potential more negative than the one at which mercury itself begins to dissolve. Therefore, we have examined the possibility of making polarographic analyses in the anodic region by substituting a platinum electrode for the dropping mercury electrode. Platinum and other noble metals having high oxygen overvoltages are, for anodic studies, in a position comparable to that of mercury for cathodic studies (see Figure 1). The range of potential covered by each type of electrode is altered by changes in the acidity of the solution.

It might be advisable at this time to point out the incompleteness of the common conception of the terms anode and cathode. In an electrolytic cell containing two similar platinum electrodes at different potentials, one of them is of necessity more negative than the other. If a reaction such as $Ag^{+} + e \rightarrow Ag^{0}$ is possible, one would expect it to take place faster though not necessarily exclusively at the electrode having the higher concentration of electrons, i.e., the more negative potential. One may draw an analagous picture for oxidation in such a cell. In contrast to this set-up, the polarographic cell usually consists of one electrode, dipping into the cell, whose potential is measured through a salt bridge against a reference electrode. The potential on the polarizable electrode within the polarographic cell can be varied continuously from strongly positive to strongly negative. This electrode is not in competition with another during a reaction. Thus in a polarographic cell, an electrode might be sufficiently negative for reduction to take place while its potential would make it an anode in the usual electrolytic cell. Therefore, "anodic" reductions and "cathodic" oxidations are quite possible in polarography. Thus, if one wishes to study the reduction of some of the stronger oxidizing agents such as permaganate, dichromate, ceric, argentous, cupric, and ferric ions, one is forced into studies of the anodic region. All of these ions are usually reduced at zero potential by

the dropping mercury electrode unless they are in the form of stable complexes which, being more difficult to reduce, require more negative potentials.

To date, several stages of development have been reached in studies of anodic reactions using stationary electrodes of noble metals. As early as 1900 electrolytic studies of the reduction of permanganate showed that as the potential became less positive a reduction current began to flow, increased with further lowering of potential, and finally flattened off in a manner exactly like the polarographic diffusion current. Other investigators showed later that many redox pairs behaved similarly, their efforts being aimed primarily at the study of reversibility of reactions or of overvoltage of different metals. The third stage was marked by the use of the polarograph by Walen and Haissinski to record the following electrolytic data automatically rather than by tediously recording each point.

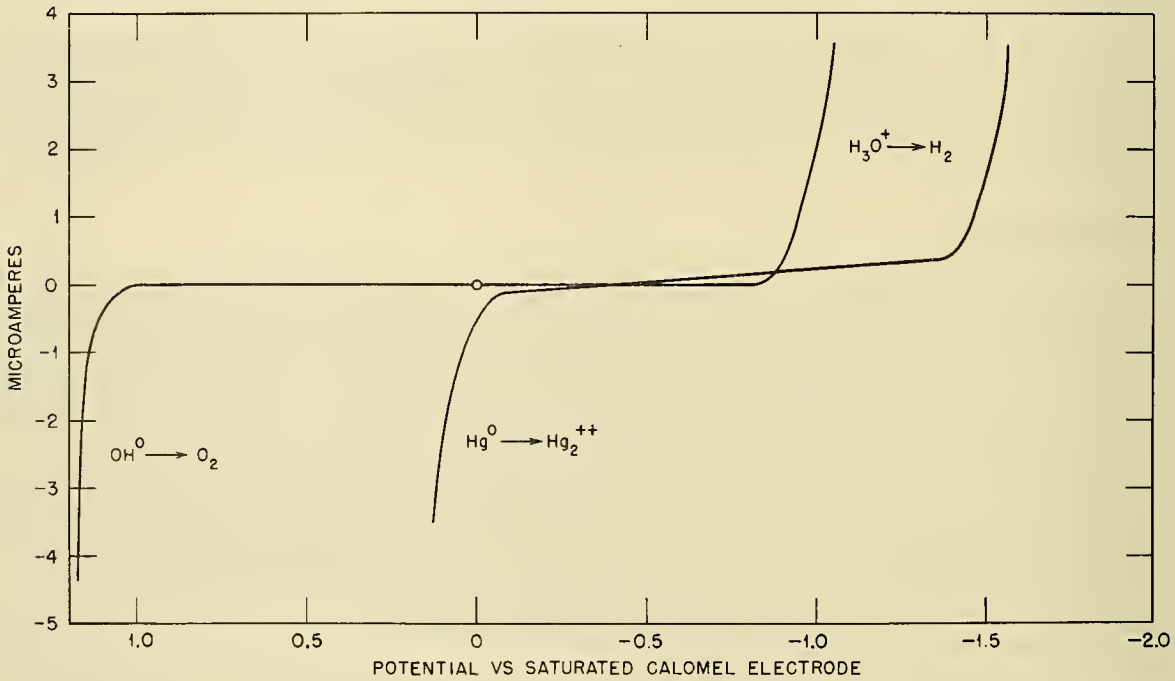

Figure 1. Ranges of potential covered by platinum and dropping mercury electrodes in neutral solutions.

In 1940, Laitinen and Kolthoff pointed out the usefulness of stationary platinum electrodes for quantitative polarography, but they used a tedious method which enabled them to proceed slowly under conditions approaching equilibrium. Each point on the polarographic curve was obtained by approaching a given potential slowly and then waiting 2 to 3 minutes for the deposition current to reach a constant value. To obtain ten points for a curve required a minimum of thirty minutes.

Laitinen and Kolthoff also reported experiments with a rotating platinum electrode which had two advantages over stationary electrodes. A constant diffusion current was reached at once, and, for a given concentration of ion, the current was much larger. Thus, the rotating electrode shortened the time required to make a curve and it reached a lower concentration of reducible ion than the station-

ary electrode. The sole disadvantage of the rotating electrode appeared to be the greater difficulty in adapting it to the analysis of small volumes of solution.

Our interest in the anodic region of potential and the desirability of using small volumes of solution prompted us to combine and to extend the work of Laitinen and Kolthoff and that of Walen and Haissinski. To date we have examined the behavior only of stationary electrodes but half-wave potentials obtained for these electrodes should be essentially the same as those for the more versatile rotating electrodes. After our work had been in progress for several months, other investigations with stationary electrodes came to our attention. Last fall Dr. O. H. Mueller reported that he had used automatic recording with stationary electrodes for his studies on mixtures of quinone and hydroquinone. By flowing the solution past the electrode he approached conditions similar to those obtained with a rotating electrode in which equilibrium is reached instantaneously. One would expect automatic recording to be feasible under these conditions. A short time ago, Dr. L. A. Matheson mentioned that he had carried out some unpublished experiments several years ago using stationary electrodes but that his studies had not proceeded beyond the preliminary stage.

We have compared the limits of reliability of data obtained with stationary electrodes using the usual automatic recording apparatus with data obtained manually according to the method of Laitinen and Kolthoff. The reliability was judged by: (1) the constancy of the half-wave potential, (2) the reproducibility of the diffusion current for a given concentration, and (3) the linearity of the relation between diffusion current and concentration. We have studied the variations introduced by using different rates of change of potential, by increasing the area of the electrode, and by stirring the solution. We selected silver ion because of its known electrochemical simplicity and reversibility, and because we expected that a reduction involving precipitation might introduce complications resulting from changes in the surface of the electrode which would be quite small if a soluble ion were produced (i.e., $Ag^{+} \rightarrow Ag^{o}$ vs $Fe^{3+} \rightarrow Fe^{2+}$).

APPARATUS

In our studies, we have used three different polarographs, Sargent Models XII and XX and a manual set-up consisting of a potentiometer, slide-wire and Rubicon galvonometer. Our polarographic cell was conventional in that the potential of the polarized electrode was measured through an agar bridge saturated with potassium nitrate against a large saturated calomel electrode. Our polarographic solution was 0.1M potassium nitrate at pH 4 containing 5×10^{-4}M silver nitrate.

RESULTS

In general, the curves had rounded maxima whose height appeared to increase with current (i.e., from higher concentrations of silver ions, or from larger electrodes). (See Figure 2.) These maxima did not appear to be of the same nature as those encountered with the dropping mercury electrode and this impression was strengthened by finding that the presence of gelatin appeared to have no effect on them. They probably result from the time-lag in reaching diffusion equilibrium. Attempts to study these maxima by varying the rate of polarization were unsuccessful because duplicate runs sometimes showed differences in behavior ranging from the usual maximum to the extreme of no maximum at all.

Although we were unable to reach a definite conclusion concerning the effect of the rate of polarization on the height of the maximum, we did find that the faster rates produced markedly larger diffusion currents (see Table 1). However, the half-wave potential appeared to be essentially unchanged regardless of the rate of polarization or the direction of polarization.

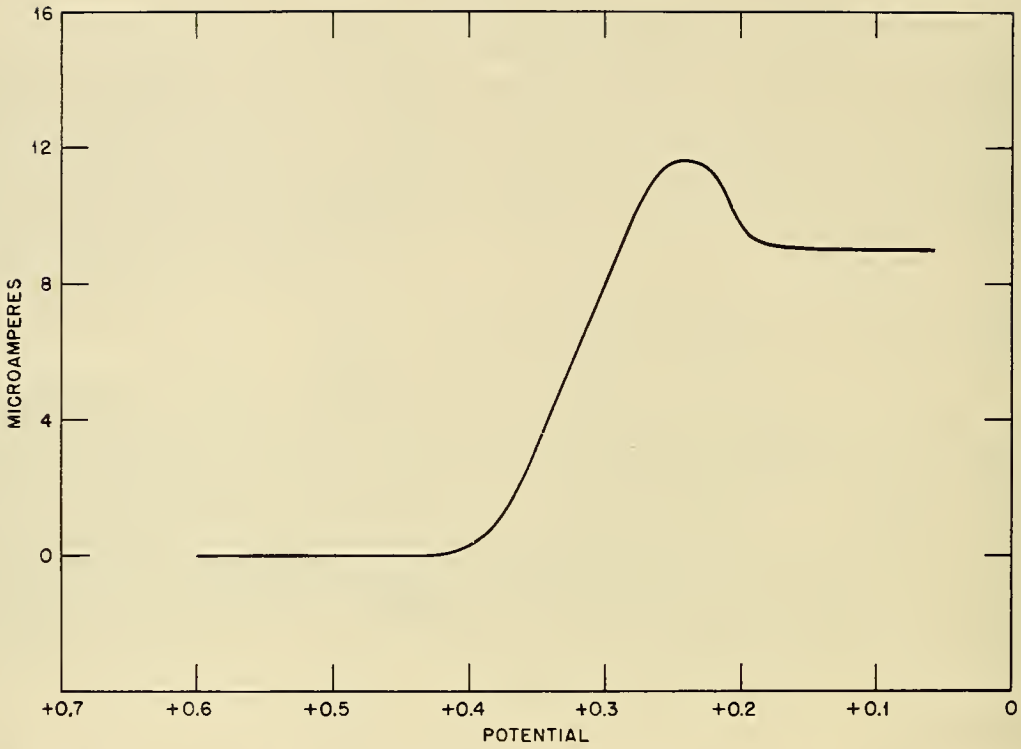

Figure 2. Reaction of silver ion at a stationary platinum electrode; recorded automatically.

Table 1. Effect of rate of polarization on diffusion current.

Rate of polarization (mv/sec)	Diffusion current (μa)	
	Quiet solutions	Stirred solutions
Manual	3.2	usually no i_d; 7.8
1.46	3.0	7.8 - 8.4
2.92	3.9	----
4.38	4.1	16.8 - 17.6

Our studies which began with the micro platinum electrode of Laitinen and Kolthoff extended to include those up to two sq cm in area. As expected, a roughly linear relation was found between electrode area and diffusion current for a given solution, but our data indicated that the behavior of electrodes became increasingly erratic with increased size. If actual unknowns were to be analyzed, it appeared to be more reliable to calibrate each electrode with a known solution rather than to depend upon calculations based on the measurement of area and current from another electrode. Despite the

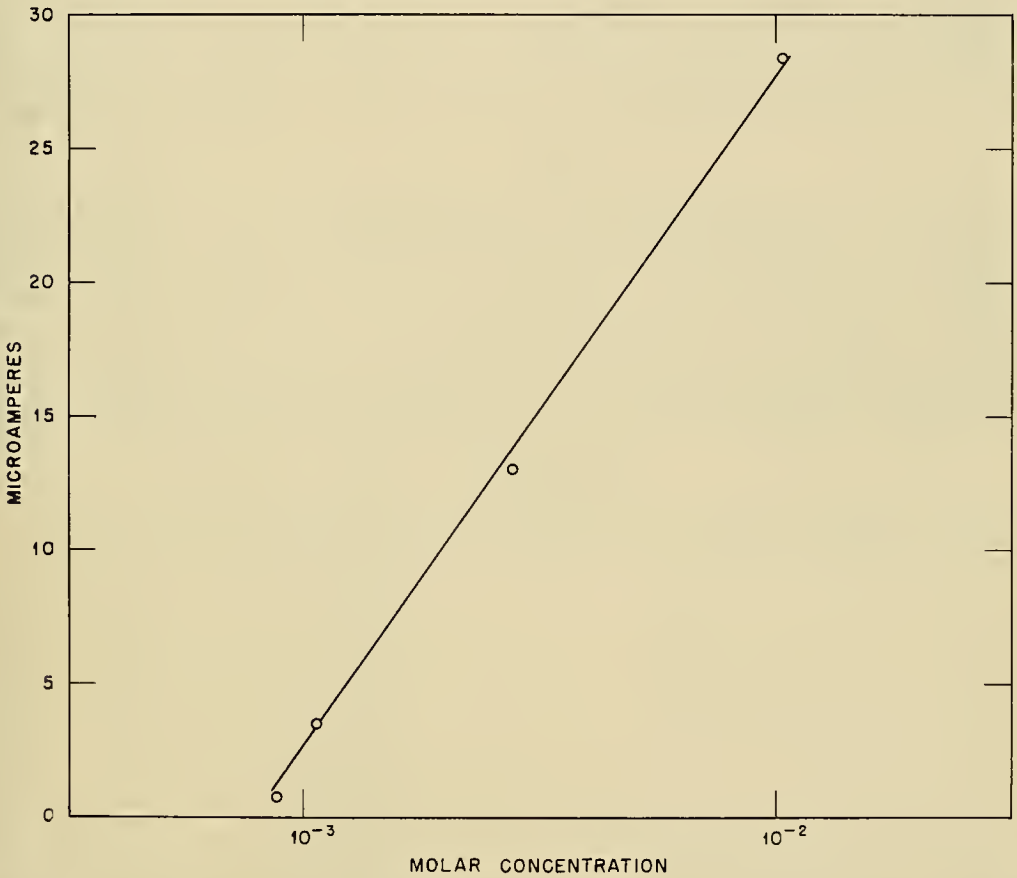

Figure 3. Relation between concentration of silver ion and diffusion current for 1 mm electrode ($0.02\ cm^{-2}$).

somewhat lower accuracy found for larger electrodes, the larger diffusion current which results from the increased area enables one to examine a lower range of concentration. This is closely analogous to the findings of Laitinen and Kolthoff concerning the better applicability to more dilute solutions of a rotating micro electrode as compared to a stationary one. Therefore, in order to cover a wider range of concentration (10^{-2} to 10^{-5}M) one should have at least two sizes of electrodes (see Figures 3, 4, and 5).

Stirring the solution completely eliminated the maximum and, as one would expect, increased the diffusion current many fold. However, while it was possible to attain 5 to 10% accuracy and precision in quiet solutions, motor stirred solutions gave results in which 20 to 30% variations were common. Thus, the method fell from semiquantitative to crudely approximate when the solution was stirred

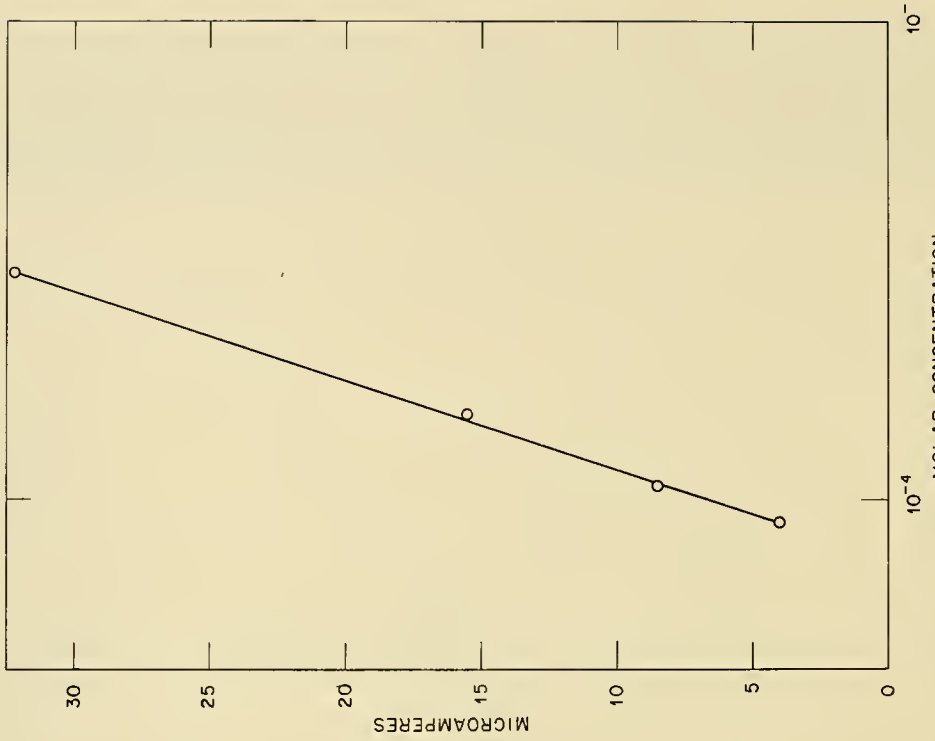

Figure 5. Relation between concentration of silver ion and diffusion current for foil electrode (2.14 cm^{-2}).

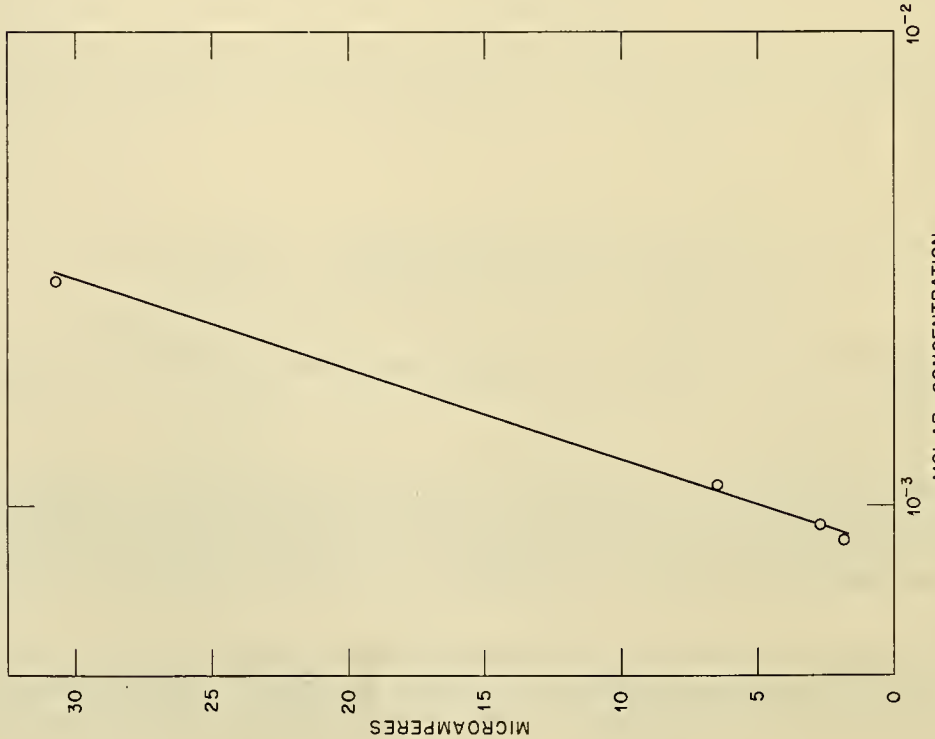

Figure 4. Relation between concentration of silver ion and diffusion current for 6 mm electrode (0.10 cm^{-2}).

under our conditions. However, in similar studies of overvoltage in which stirred solutions were employed, much better precision was obtained. Rotating electrodes also give better agreement and appear to be easier to control although they are more difficult to set up initially than a simple stirrer.

Discussion

The studies which have been discussed up to this point were made on the silver nitrate solution described at the beginning. Half-wave potentials for ions other than silver which are reduced at a stationary platinum anode are shown in Table 2. Curves for permanganate and dichromate are shown in Figures 6 and 7. Although our studies are not complete, we have evidence that, in every case, a linear relation between diffusion current and concentration should be found. Our studies of these ions together with others falling in the anodic region have been examined by us in some detail and will be reported at some time in the future.

Before attempting to interpret results obtained with stationary electrodes by continuous recording one should recognize several factors which will have important bearing upon the results. First, it is essential that the electrodes be quickly and reproducibly cleaned, and this can be done easily by chemical methods. However, an electrode can sometimes be cleaned following a run by simply changing (usually reversing) its potential. The selection of the proper potential is sometimes difficult because the use of extreme potentials for cleaning often produces waves having different diffusion currents and sometimes different half-wave potentials (see Figure 8). These variations appear to result from the presence of films of oxygen or hydrogen which were produced on the electrode during the cleaning. Finally, one must face the fact that if a reaction is irreversible, potential alone may not be able to accomplish the cleaning job.

Table 2. Half-wave potentials of some ions reduced at a stationary platinum anode.

0.1M H_2SO_4	
Ce^{4+}	~+0.45
IO_4^-	+0.65
$CrO_4^=$	+0.45; +0.13
MnO_4^-	+0.87
0.1M HCl	
Cu^{++}	+0.09; −0.21
Fe^{3+}	+0.52

The question of irreversibility is also important when half-wave potentials are recorded since, in instances analagous to those known for the dropping mercury electrode, a wave found at a certain potential using one direction of polarization may be displaced as much as 1 or 2 tenths of a volt—or may even be absent altogether—when the direction of polarization is reversed (Figure 9). Likewise, one should not expect that all half-wave potentials obtained with platinum will necessarily agree with those obtained with the mercury electrode. The source of the disagreement undoubtedly arises from the difficulty in determining whether or not an electrode is truly inert.

Lastly, the fact that maxima are the rule, rather than the exception means that one is more limited than usual in obtaining reliable diffusion currents and good definition of waves when two components of a mixture have half-wave potentials which are nearly alike. Better results might be obtained under such circumstances using very slow rates of polarization. A rotating electrode or the use of stirred solutions would, of course, eliminate the maxima.

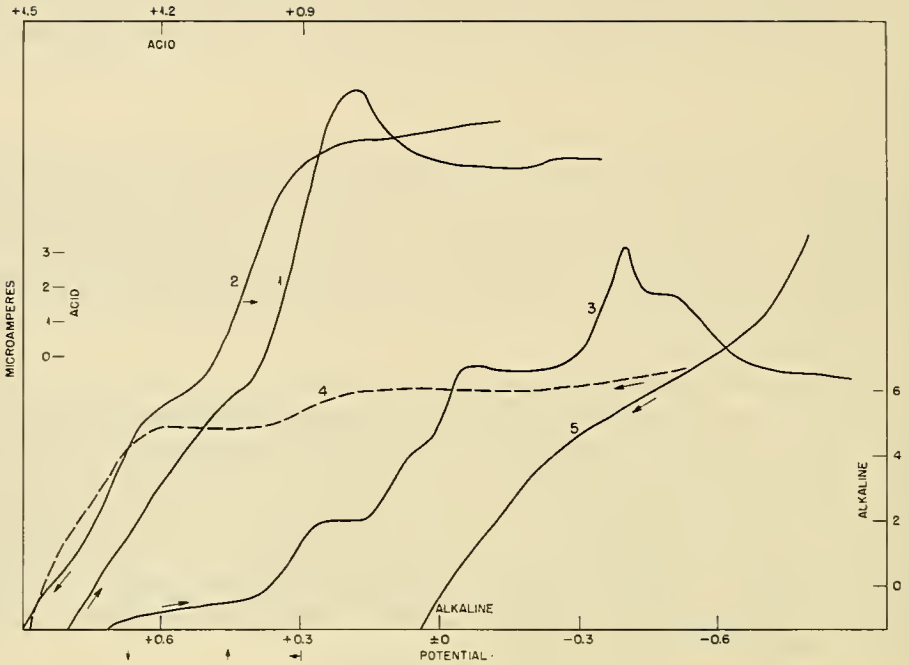

Figure 6. (1) (2) Reduction of MnO_4^- in 0.1M H_2SO_4, (3) (5) reduction of MnO_4^- in 0.1M NaOH, (4) oxidation of Mn^{++} in 0.1M H_2SO_4. All solutions were 10^{-3}M Mo.

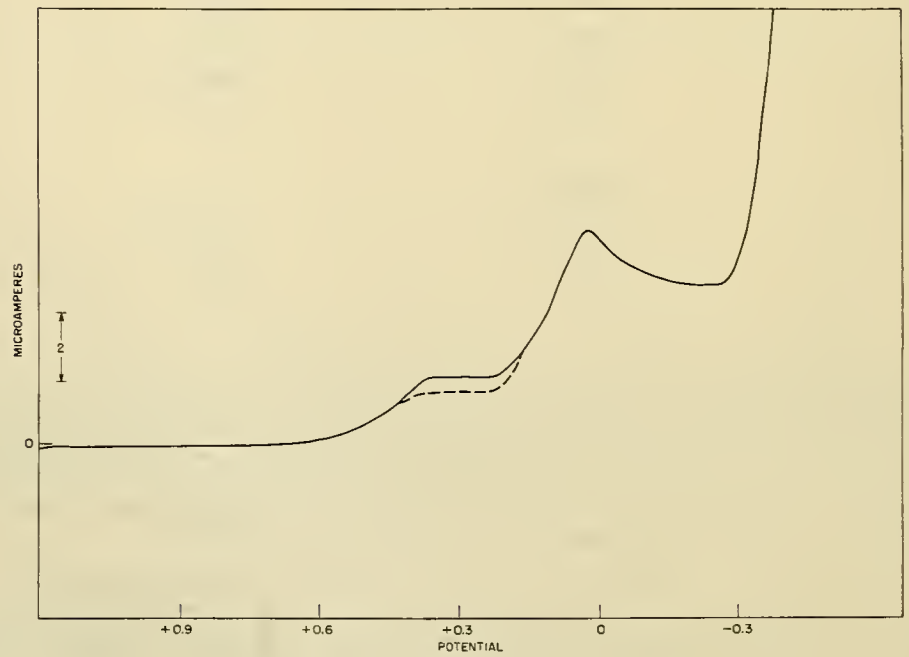

Figure 7. Reduction of 10^{-3}M $CrO_4^=$ in 0.1M H_2SO_4.

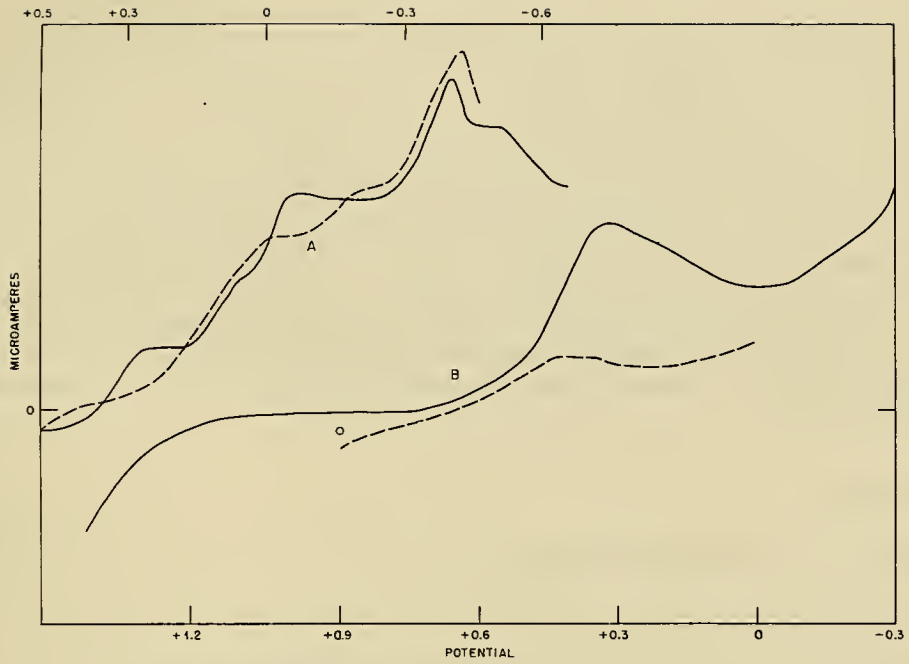

Figure 8. Cleaning electrode by potential—

A - alkaline MnO_4^- — Chemical --- Potential

B - ReO_4^- in H_2SO_4 —— Very positive potential (+1.5 v) --- At 0.2 v more positive than starting potential

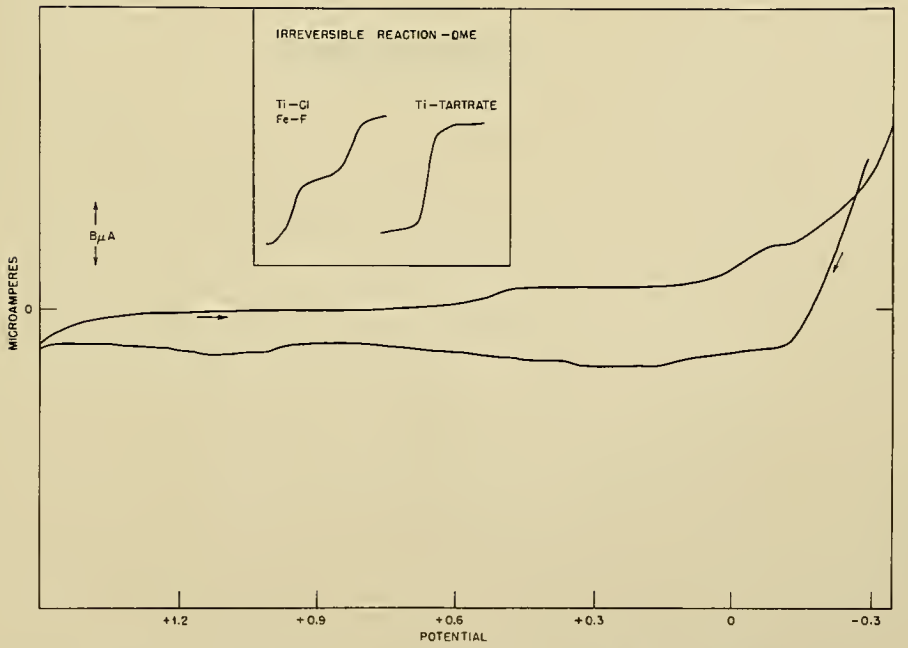

Figure 9. Irreversible reaction—platinum electrode 10^{-3}M ReO_4^- (*) in 2N H_2SO_4.

*Waves due partly to impurities in H_2SO_4.

In concluding this discussion, some of the advantages of solid electrodes might be mentioned briefly. As mentioned earlier, a knowledge of the behavior of solid electrodes enables one to obtain very rapidly information which is useful, not only to polarographers, but also to those interested in carrying out electrolyses. Users of the Sargent Model XX Polarograph in particular may find some satisfaction in the fact that one does not encounter huge oscillations in the record but instead a smooth and comparatively unambiguous line. Of real importance to all polarographers are the possibilities for rapidly examining many inorganic and organic compounds in the anodic region. Furthermore, solid electrodes as opposed to dropping mercury electrodes allow analyses to be made under otherwise difficult or impossible conditions, namely, in fused salts or in nonaqueous solvents (liquid ammonia) in low temperatures. As pointed out earlier, our studies dealt with stationary electrodes because they seem to be most suitable for anodic studies involving micro volumes of solution. However, extension of our information to rotating electrodes should be simple, and the use of rotating electrodes whenever the volume of solution permits should give an increase in sensitivity and in definition of waves.

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